A METHOD FOR SUPERCRITICAL CARBON DIOXIDE PROCESSING OF FLUORO-CARBON FILMS

DESCRIPTION

FIELD OF THE INVENTION

[Para 1] The present invention relates to the field of processing dielectric films and, more particularly, to supercritical carbon dioxide processing of fluoro-carbon films for integration of the films into semiconductor devices.

BACKGROUND OF THE INVENTION

[Para 2] The drive to reduce the minimum feature sizes of microelectronic devices to meet the demand for faster, lower power microprocessors and digital circuits has introduced new materials and processes into device manufacturing. These new materials include low dielectric constant (low-k) materials and ultra-low-k (ULK) materials that can provide several advantages relative to the traditional silicon dioxide dielectric materials. For example, the use of low-k fluoro-carbon materials to separate conductive lines in semiconductor devices reduces the RC time constant by reducing the capacitance, which in turn, increases the speed of the device.

[Para 3] Fluoro-carbon films have attracted a great deal of interest not only as material for interlayer dielectrics in ultra-large scale integrated (ULSI) circuits, but also for electrical insulation in electrical equipment, because of their low dielectric constant, high-dielectric strength, and chemical inertness. Although low-k fluoro-carbon materials have a number of advantageous properties, they tend to be less chemically robust than more traditional oxide and nitride dielectric layers and they can suffer from problems that limit their use in typical semiconductor processes. These problems include outgassing (e.g., fluorine outdiffusion) and undesirable chemical reactions during processing, and poor adhesion to other materials in the semiconductor device.

SUMMARY OF THE INVENTION

[Para 4] The present invention provides a method for processing a fluoro-carbon dielectric film for integration of the dielectric film into a semiconductor device.

[Para 5] According to an embodiment of the invention, the method includes providing a substrate having a fluoro-carbon film deposited thereon, the film having an exposed surface containing contaminants, and treating the exposed surface with a supercritical carbon dioxide fluid to clean the exposed surface of the contaminants and provide surface termination.

[Para 6] According to another embodiment of the invention, the method includes providing a substrate having a patterned fluoro-carbon dielectric film formed thereon, the patterned fluoro-carbon dielectric film having one or more vias, trenches, or combinations thereof, and the patterned fluoro-carbon dielectric film having an exposed surface containing contaminants; and treating the exposed surface with a supercritical carbon dioxide fluid to clean the exposed surface of the contaminants and provide surface termination.

[Para 7] According to an embodiment of the invention, the supercritical carbon dioxide treatment improves adhesion and annealing properties of a metal-containing film formed on the surface of a treated fluoro-carbon dielectric film.

BRIEF DESCRIPTION OF THE DRAWINGS

[Para 8] In the accompanying drawings:

[Para 9] FIGS. 1A – 1B show a cross-sectional view of a process of treating a film structure containing a fluoro-carbon dielectric film in accordance with an embodiment of the invention;

[Para 10] FIG. 1C shows a cross-sectional view of a film structure containing a metal-containing layer on a treated fluoro-carbon dielectric film in accordance with an embodiment of the invention;

[Para 11] FIG. 1D shows a cross-sectional view of a patterned film structure containing a treated fluoro-carbon dielectric film in accordance with another embodiment of the invention;

[Para 12] FIG. 2 is a flow diagram for supercritical carbon dioxide processing of a fluoro-carbon dielectric film according to an embodiment of the present invention;

[Para 13] FIG. 3 shows a simplified schematic diagram of a supercritical carbon dioxide processing system in accordance with an embodiment of the invention;

[Para 14] FIG. 4 is a plot of pressure versus time for supercritical carbon dioxide processing of a fluoro-carbon dielectric film in accordance with an embodiment of the invention;

[Para 15] FIG. 5 is a flow diagram for supercritical carbon dioxide processing of a fluoro-carbon dielectric film in accordance with an embodiment of the invention; and

[Para 16] FIG. 6 shows electrical resistance measurements of film structures containing tantalum films deposited onto fluoro-carbon dielectric films processed according to embodiments of the present invention.

DETAILED DESCRIPTION OF SEVERAL EMBODIMENTS OF THE INVENTION

[Para 17] FIGS. 1A – 1B show a cross-sectional view of a process for treating a film structure containing a fluoro-carbon dielectric film in accordance with an embodiment of the invention. The film structure 1 contains a substrate 2 and a fluoro-carbon dielectric film 4 deposited onto the substrate 2. The fluoro-carbon dielectric film 4 can, for example, be a dense film with low or no porosity. In one example, the fluoro-carbon dielectric film can have dielectric constant between about 2.2 and about 2.4. Low porosity of the fluoro-carbon dielectric film 4 can reduce or eliminate various problems, such as moisture uptake and poor mechanical strength, which are commonly encountered for porous low-k films. The fluoro-carbon dielectric film 4 can, for example, be deposited on the substrate 2 in a plasma processing system using a process gas containing a halocarbon gas (e.g., C_5F_8 or $SiH(CH_3)_3$).

[Para 18] In one example, the fluoro-carbon dielectric film 4 can be deposited using a radial line slot antenna (RLSA) plasma source for 2.45 GHz-microwave using a process gas containing a C_5F_8 gas flow rate of 250 standard cubic centimeters per second (sccm) and an Ar gas flow rate of 200 sccm at a process gas pressure of 45 mTorr in the plasma processing chamber. The plasma power can, for example, be about 2,300 W; the temperature of the substrate 2 can, for example, be about 350ºC; and the thickness of the fluoro-carbon film can, for example, be about 1500 – 3000 Å. As would be appreciated by those skilled in the art of plasma processing, other plasma sources and process gases can be used to deposit the fluoro-carbon dielectric film 4 onto the substrate 2.

[Para 19] In another example, nitrogen can be incorporated into the deposited fluoro-carbon dielectric film 4. The nitrogen-incorporation, for example, be performed by a RLSA plasma source using a process gas containing a N_2 gas at a gas flow rate of 50 sccm and a process gas pressure of 250 mTorr in the plasma processing chamber. The plasma power can, for example, be about 1,500 W; the temperature of the substrate 2 can, for example, be about 350ºC; and the processing time can be about 1 min.

[Para 20] The fluoro-carbon dielectric film 4 can contain contaminants 8 on the exposed surface 6. The contaminants 8 can, for example, originate from the process of depositing the fluoro-carbon dielectric film 4 onto the substrate 2 and/or from post-deposition exposure of the fluoro-carbon dielectric film 4 to contaminants. In one embodiment of the invention, the contaminants 8 can contain a thin layer (e.g., less than 100 angstroms (Å)) of hydrocarbon fragments (e.g., CH_x), water (H_2O), hydroxyl (OH), or hydrogen fluoride (HF), or a combination of two or more thereof. Fourier-transform infrared (FTIR) spectroscopy of as-deposited fluoro-carbon dielectric films from halocarbon gas showed the presence of C-H functional groups on the surface 6. The presence of the contaminants 8 on the surface 6 can lead to poor adhesion of metal-containing films and other films to the fluoro-carbon dielectric film 4, as well as other integration problems.

[Para 21] FIG. 1B shows the film structure 1 following supercritical carbon dioxide processing of the fluoro-carbon dielectric film 2 according to an embodiment of the present invention. The supercritical carbon dioxide processing is capable of cleaning at least a portion of the contaminant 8 from the surface 6 of the fluoro-carbon dielectric film 4, and can provide surface termination of the fluoro-carbon film 4 by forming a surface termination layer 10. In one embodiment of the invention, the supercritical carbon dioxide processing can use pure supercritical carbon dioxide fluid to form a surface termination layer 10 containing C-F functional groups. In another embodiment

of the invention, the supercritical carbon dioxide fluid can include an alcohol. The alcohol can, for example, contain methanol, ethanol, propanol, or butanol, or a combination of two or more thereof.

[Para 22] In yet another embodiment of the invention, the supercritical carbon dioxide processing can use a supercritical carbon dioxide fluid containing a silicon-containing chemical to form a surface termination layer 10 containing $Si-CH_3$ functional groups. The silicon-containing chemical can be selected from a wide variety of compounds, for example, hexamethyldisilane, hexamethyldisilazane, dimethylsilyldiethylamine, tetramethyldisilazane, trimethylsilyldimethylamine, dimethylsilyldimethylamine, trimethylsilyldiethylamine, bis-trimethylsilyl-urea, bis(dimethylamino)methyl silane, bis(dimethylamino)dimethyl silane, dimethylaminopentamethyldisilane, dimethylaminodimethyldisilane. In still another embodiment of the invention, the supercritical carbon dioxide fluid can contain an alcohol and a silicon-containing chemical. As would be appreciated by those skilled in the art, other alcohols and silicon-containing chemicals may be employed without departing from the scope of the invention. For example, the silicon-containing chemicals can generally contain silanes, disilanes, silyl amines, silyl ureas, and silazanes.

[Para 23] FTIR spectroscopy of fluoro-carbon dielectric films treated according to embodiments of the invention showed removal of C-H functional groups from the surface 6. In addition, the supercritical carbon dioxide processing was found to preserve various material properties of the film 4, including the dielectric constant, the refractive index, the modulus, and the hardness, and the film thickness. Furthermore, the supercritical carbon dioxide processing was found to reduce leakage current density of the processed films by about one order of magnitude, compared to the as-deposited films.

[Para 24] FIG. 1C shows a cross-sectional view of a film structure containing a metal-containing layer on a treated fluoro-carbon dielectric film in accordance with an embodiment of the invention. In FIG. 1C, the film structure 1 contains a metal-containing film 12 deposited onto the surface termination layer 10. The metal-containing film 12 can, for example, be a tantalum-containing film. The tantalum-containing film can contain Ta, TaN_x, or a combination thereof. In one example, the tantalum-containing film can contain a layered Ta, TaN_x structure. The metal-containing film can, for example, be a barrier layer, such as diffusion barrier layer for copper metallization.

[Para 25] Supercritical carbon dioxide processing of the fluoro-carbon dielectric film 4 according to embodiments of the invention was found to provide improved adhesion of the metal-containing film 12 to the fluoro-carbon film 4. Furthermore, the supercritical carbon dioxide processing resulted in improved electrical resistivity of the film structure 1 before and after annealing of the film structure 1 shown in FIG. 1C.

[Para 26] FIG. 1D shows a cross-sectional view of a patterned film structure containing a treated fluoro-carbon dielectric film in accordance with another embodiment of the invention. The patterned film structure 20 contains examples of horizontal and vertical surfaces of a fluoro-carbon dielectric film encountered in semiconductor processing. The film structure 20 contains a substrate 22, a metal film 24, a fluoro-carbon dielectric film 26, a surface termination layer 28, a metal-containing barrier layer 30, and a metal film 32.

[Para 27] FIG. 2 is a flow diagram for supercritical carbon dioxide processing of a fluoro-carbon dielectric film according to an embodiment of the present invention. Referring additionally to FIGS. 1A – 1B, the process 200 includes, in step 202, providing in a supercritical processing system a substrate 2 having a fluoro-carbon dielectric film 4 deposited thereon. The film 4 has an exposed surface 6 containing contaminants 8. Next, in step 204, the process 200 includes treating the surface 6 with a supercritical carbon dioxide fluid to clean the surface 6 of the contaminants 8 and provide a surface termination layer 10. The process 200 can be used to process horizontal as well as vertical surfaces of fluoro-carbon dielectric films. Via and trench sidewalls are examples of vertical surfaces encountered in semiconductor processing, for example dual damascene processing.

[Para 28] It will be clear to one skilled in the art that each of the steps or stages in the flowchart of FIG. 2 may encompass one or more separate steps and/or operations. Accordingly, the recitation of only two steps in 202, 204 in the process 200, should not be understood to be limited solely to two steps or stages. Moreover, each representative step or stage 202, 204 should not be understood to be limited to only a single process.

[Para 29] FIG. 3 shows a simplified schematic diagram of a supercritical carbon dioxide processing system in accordance with an embodiment of the invention. The processing system 100 contains a substrate transfer system 170 configured to move a substrate 105 in and out of the process chamber 108 of a process module 110 through a slot (not shown). In one example, the slot can be opened and closed by moving the chuck 118, and in another example, the slot can be controlled using a gate valve (not

shown). In FIG. 3, the processing system 100 further includes a circulation system 120, a chemical supply system 130, a carbon dioxide supply system 140, a pressure control system 150, an exhaust system 160, and a controller 180. The controller 180 can be coupled to the processing module 110, the circulation system 120, the chemical supply system 130, the carbon dioxide supply system 140, the pressure control system 150, the exhaust system 160, and the substrate transfer system 170. Alternately, the controller 180 can be coupled to a one or more additional controllers/computers (not shown), and the controller 180 can obtain setup and/or configuration information from an additional controller/computer.

[Para 30] In FIG. 3, singular processing elements (110, 120, 130, 140, 150, 160, 170, and 180) are shown, but this is not required for the invention. The processing system 100 can include any number of processing elements having any number of controllers associated with them in addition to independent processing elements. The controller 180 can be used to configure any number of processing elements (110, 120, 130, 140, 150, 160, and 170), and the controller 180 can collect, provide, process, store, and display data from the processing elements. The controller 180 can comprise a number of applications for controlling one or more of the processing elements. For example, controller 180 can include a GUI (graphic user interface) component (not shown) that can provide easy to use interfaces that enable a user to monitor and/or control one or more processing elements.

[Para 31] The processing module 110 can include an upper assembly 112, a frame 114, and a lower assembly 116. The upper assembly 112 can comprise a heater (not shown) for heating the process chamber 108, the substrate 105, or the supercritical carbon dioxide fluid, or a combination of two or more thereof. Alternately, a heater is not required. The frame 114 can include means for flowing a supercritical carbon dioxide fluid through the process chamber 108. In one example, a circular flow pattern can be established in the process chamber 108; and in another example, a substantially linear flow pattern can be established in the process chamber 108. Alternately, the means for flowing a processing fluid in the process chamber 108 can be configured differently. The lower assembly 116 can comprise one or more lifters (not shown) for moving the chuck 118 and/or the substrate 105. Alternately, a lifter is not required.

[Para 32] In one embodiment, the processing module 110 includes a holder or chuck 118 for supporting and holding the substrate 105 while processing the substrate 105. The stage or chuck 118 can also be configured to heat or cool the substrate 105 before, during, and/or after processing the substrate 105. Alternately, the processing module 110 can include a platen (not shown) for supporting and holding the substrate

105 while processing the substrate 105. The process chamber 108 can process a substrate 105 of any size, for example a 200 mm substrate, a 300 mm substrate, or an even larger substrate.

[Para 33] The circulation system 120 can comprise one or more valves for regulating the flow of a supercritical carbon dioxide fluid through the circulation system 120 and through the processing module 110. The circulation system 120 can comprise any number of back-flow valves, filters, pumps, and/or heaters (not shown) for maintaining and flowing a supercritical carbon dioxide fluid through the circulation system 120 and through the processing module 110. Carbon dioxide fluid is in a supercritical state when above the critical temperature T_c of about 31°C and the critical pressure P_c of about 1,070 psig. Supercritical carbon dioxide fluid has virtually no viscosity or surface tension and has therefore no difficulty in penetrating all the way to the bottom of a micro-feature to remove a residue from the micro-feature. In one embodiment of the invention, the temperature of the supercritical carbon dioxide fluid in the process chamber 108 can be between about 35°C and about 200°C. Alternately, the temperature of the carbon dioxide fluid in the process chamber 108 can be between about 40°C and about 120°C.

[Para 34] The processing system 100 can contain a carbon dioxide supply system 140. As shown in FIG. 3, the carbon dioxide supply system 140 can be coupled to the processing module 110, but this is not required. In alternate embodiments, the carbon dioxide supply system 140 can be configured differently and coupled differently. For example, the carbon dioxide supply system 140 can be coupled to the circulation system 120.

[Para 35] The carbon dioxide supply system 140 can contain a carbon dioxide source (not shown) and a plurality of flow control elements (not shown) for controlling delivery of carbon dioxide fluid to the process chamber 108. For example, the carbon dioxide source can include a carbon dioxide feed system, and the flow control elements can include supply lines, valves, filters, pumps, and heaters. The carbon dioxide supply system 140 can comprise an inlet valve (not shown) that is configured to open and close to allow or prevent the stream of carbon dioxide from flowing into the process chamber 108. For example, controller 180 can be used to determine fluid parameters including pressure, temperature, process time, and flow rate.

[Para 36] In the illustrated embodiment in FIG. 3, the chemical supply system 130 is coupled to the circulation system 120, but this is not required for the invention. In alternate embodiments, the chemical supply system 130 can be configured differently

and can be coupled to different elements in the processing system 100. The chemical supply system 130 can comprise a cleaning chemical assembly (not shown) for providing a cleaning chemical for generating a supercritical carbon dioxide fluid with a desired concentration of cleaning chemicals within the process chamber 108. The cleaning chemicals can, for example, include solvents such as alcohols and/or silicon-containing chemicals. By way of further example, the cleaning chemicals can include methanol, hexamethyldisilane, or both.

[Para 37] The chemical supply system 130 can furthermore provide a rinsing chemical for generating supercritical carbon dioxide rinsing fluid within the process chamber 108. The rinsing chemical can include one or more organic solvents including, but not limited to, alcohols, ketones, or both. In one embodiment of the invention, the organic solvent can contain methanol, ethanol, n-propanol, isopropanol, benzyl alcohol, acetone, butylene carbonate, propylene carbonate, dimethylsulfoxide, γ-butyrolactone, dimethyl formamide, dimethyl acetamide, or ethyl lactate, or a combination of two or more thereof. As would be appreciated by those skilled in the art, other organic solvents may be employed without departing from the scope of the invention.

[Para 38] The processing system 100 can also comprise a pressure control system 150. As shown in FIG. 3, the pressure control system 150 can be coupled to the processing module 110, but this is not required. In alternate embodiments, pressure control system 150 can be configured differently and coupled differently. The pressure control system 150 can include one or more pressure valves (not shown) for regulating the pressure within the process chamber 108. Alternately, the pressure control system 150 can also include one or more pumps (not shown). For example, one pump may be used to increase the pressure within the process chamber, and another pump may be used to evacuate the process chamber 108. In another embodiment, the pressure control system 150 can comprise means for sealing the process chamber. In addition, the pressure control system 150 can comprise means for raising and lowering the substrate 105 and/or the chuck 118.

[Para 39] Furthermore, the processing system 100 can comprise an exhaust system 160. As shown in FIG. 3, the exhaust system 160 can be coupled to the processing module 110, but this is not required. In alternate embodiments, exhaust system 160 can be configured differently and coupled differently. The exhaust system 160 can include an exhaust gas collection vessel (not shown) and can be used to remove contaminants from the processing fluid. Alternately, the exhaust system 160 can be used to recycle the processing fluid.

[Para 40] Controller 180 can be used to feed forward and/or feed back information. For example, feed-forward information can comprise pre-process data associated with an in-coming substrate. This pre-process data can include lot data, batch data, run data, type of substrate, and type of layers overlying the substrate, and history data including, for example, type of process gases used in depositing a fluoro-carbon dielectric film on the substrate. The pre-process data can be used to establish an input state for a substrate. The controller 180 can use the difference between an input data item for an incoming substrate (input state) and a desired data item (desired state) to predict, select, or calculate a set of process parameters to achieve the desired result of changing the state of the substrate from the input state to the desired state. The desired state can, for example, indicate the level of substrate cleanliness following a cleaning process and/or a rinse process. For example, this predicted set of process parameters can be a first estimate of a recipe to use based on an input state and a desired state. In one embodiment, data such as the input state and/or the desired state data can be obtained from a host.

[Para 41] In one example, the controller 180 knows the input state and a model equation for the desired state for the substrate, and the controller determines a set of recipes that can be performed on the substrate to change the status of the substrate from the input state to a desired state. For example, the set of recipes can describe a multi-step process involving a set of process systems. For example, post-process metrology data can be obtained to evaluate the state of the substrate, i.e., if the contaminant has been sufficiently removed from the fluoro-carbon dielectric film. Post-process metrology data can be obtained after a time delay that can vary from minutes to days. Post-process metrology data can be used as a part of the feedback control.

[Para 42] The controller 180 can compute a predicted state for the wafer based on the input state, the process characteristics, and a process model. For example, a cleaning rate model can be used along with a contaminant level to compute a predicted cleaning time. Alternately, a rinse rate model can be used along with a contaminant level to compute a processing time for a rinse process. The controller 180 can comprise a database component (not shown) for storing input and output data. Process models can include linear models, quadratic models, full quadratic models, and higher order polynomial models. A process model can provide the relationship between one or more process recipe parameters or setpoints and one or more process results and can include multiple variables.

[Para 43] In a supercritical cleaning/rinsing process, the desired process result can be a process result that is measurable using an optical measuring device. For

example, the desired process result can be an amount of contaminant on a fluoro-carbon dielectric film. After each cleaning process run, an actual process result can be measured and compared to a desired process result to determine process compliance. After each cleaning process run, the actual process results can be determined, and a system of equations can be created to solve for the coefficients in the model equation.

[Para 44] In general, process control can include updating a process module recipe using metrology information measured on the substrate prior to its arrival in the process module 110. For a cleaning process, the incoming substrates should all be the same, with the same pre-processing data. The controller can use the pre-processing data to verify that all of the substrates used in a group are the same. The process of creating the process models requires an understanding of the mechanics of experimental design, execution of an appropriate experiment and analysis of the resultant experimental data. This process can be highly automated and integrated into the film removal system 70 using the technique described herein.

[Para 45] FIG. 4 is a plot of pressure versus time for supercritical carbon dioxide processing in accordance with an embodiment of the invention. In FIG. 4, a substrate having a fluoro-carbon dielectric film deposited thereon, wherein the film has an exposed surface containing contaminants, is placed in a supercritical fluid process chamber at an initial time T_0. The process chamber can, for example, be process chamber 108 of the supercritical carbon dioxide processing system 100 in FIG. 3. During the time period T_1, the process chamber 108 is pressurized to generate a supercritical carbon dioxide fluid and to reach the desired operating pressure (P_{op}). When the carbon dioxide pressure within the process chamber 108 reaches or exceeds the critical pressure P_c (1,070 psig for carbon dioxide at 31ºC) at time T_1', one or more cleaning chemicals can be injected into the process chamber 108 from chemical supply system 130. The cleaning chemical can, for example, include an alcohol, a silicon-containing chemical, or both, as described above. Several injections of cleaning chemicals can be performed to generate a supercritical carbon dioxide fluid with the desired concentrations of cleaning chemicals. Alternately, the cleaning chemicals can be injected into the process chamber 108 after the time T_1'. In another embodiment of the invention, the supercritical fluid can contain pure carbon dioxide.

[Para 46] When the pressure within the process chamber 108 reaches an operating pressure P_{op} at the start of time period T_2, the supercritical carbon dioxide fluid is circulated over and/or around the substrate 105 and through the process chamber 108 using the circulation system 120, such as described above. The operating pressure P_{op} can be any value as long as the pressure is sufficient to maintain supercritical fluid

conditions and can, for example, be about 2,800 psig. The length of the time period T_2 can be selected to sufficiently clean contaminants from the substrate 105.

[Para 47] Next, a push-through process can be carried out during time period T_3, where a fresh stock of supercritical carbon dioxide fluid is fed into the process chamber 108 from the carbon dioxide supply system 140, thereby increasing the pressure in the process chamber 108. Furthermore, during the push-through process in period T_3, the supercritical carbon dioxide fluid, along with any process residue suspended or dissolved therein, is simultaneously displaced from the process chamber 108 using the exhaust system 160.

[Para 48] The push-through process reduces the amount of particulates and contaminants that can fall-out from the supercritical carbon dioxide fluid when its composition is altered by adding the fresh stock of supercritical carbon dioxide fluid. A number of methods for reducing fall-out of particles and contaminants using push-through techniques and/or pressurization techniques are described in U.S. Patent Application No. 10/338,524, filed January 7, 2003, titled "METHOD FOR REDUCING PARTICULATE CONTAMINATION IN SUPERCRITCIAL FLUID PROCESSING", and U.S. Patent Application No. 10/394,802, filed March 21, 2003, titled "REMOVAL OF CONTAMINANTS USING SUPERCRITICAL PROCESSING", both of which are hereby incorporated by reference in their entirety.

[Para 49] When the push-through step is complete at the end of time period T_3, a plurality of decompression and compression cycles can be performed in the process chamber 108 during time period T_4 to further remove contaminants from the substrate 105 and the supercritical fluid processing system. The decompression and compression cycles can be performed using the exhaust system 160 to lower the process chamber pressure to below the operating pressure P_{op} and then injecting fresh supercritical carbon dioxide fluid to raise the process chamber pressure to above the operating pressure P_{op}. The decompression and compression cycles allow the cleaning chemicals and any removed residue to be removed from the system before the next processing step. The supercritical cleaning steps are repeated as needed with the same or different cleaning chemicals. After a pre-determined number of the decompression and compression cycles are completed (four cycles are shown in FIG. 4), the process chamber 108 can be vented and exhausted to atmospheric pressure through the exhaust system 160. Thereafter, the substrate 105 can be removed from the process chamber 108 by the substrate transfer system 170 and the next substrate loaded into the process chamber 108. Alternately, the processed substrate 105 can be exposed to a supercritical carbon dioxide rinsing solution in the process chamber 108 before the substrate is removed from the process chamber 108.

[Para 50] The graph shown in FIG. 4 is provided for exemplary purposes only. It will be understood by those skilled in the art that a supercritical processing step can have any number of different time/pressures or temperature profiles without departing from the scope of the present invention. Furthermore, any number of cleaning and rinse processing sequences with each step having any number of compression and decompression cycles are contemplated. In addition, as stated previously, concentrations of various chemicals and species within a supercritical carbon dioxide fluid can be readily tailored for the application at hand and altered at any time within a supercritical cleaning process.

[Para 51] FIG. 5 is a flow diagram for supercritical carbon dioxide processing of a fluoro-carbon dielectric film in accordance with an embodiment of the invention. The process 500 includes, in step 502, placing a substrate having a fluoro-carbon dielectric film deposited thereon in a process chamber, wherein the exposed surface of the fluoro-carbon dielectric film contains contaminants. After the substrate is placed in the process chamber, in step 504 carbon dioxide is added to the process chamber, which is then pressurized to generate supercritical carbon dioxide fluid, and a cleaning chemical is optionally added to the supercritical carbon dioxide fluid. Alternately, the cleaning chemical may be omitted from the supercritical carbon dioxide fluid. After the supercritical carbon dioxide fluid is generated in step 504, the substrate is maintained in the supercritical carbon dioxide fluid in step 506 for a period of time sufficient to remove at least a portion of the contaminants from the fluoro-carbon dielectric film. During the step 506, the supercritical carbon dioxide fluid can be circulated through the process chamber and/or otherwise agitated to move the supercritical carbon dioxide fluid over surfaces of the substrate.

[Para 52] Still referring to FIG. 5, after at least a portion of the contaminants is removed from fluoro-carbon dielectric film in step 506, the process chamber is partially exhausted at 508. The steps 504 - 508 can be repeated any number of times required to remove a portion of the contaminants from the fluoro-carbon dielectric film, as indicated in the flow diagram. In accordance with embodiments of the invention, repeating steps 504 and 506 can use fresh supercritical carbon dioxide, fresh chemicals, or both. Alternately, the concentration of the process chemicals in the supercritical carbon dioxide fluid can be modified by diluting the fluid with supercritical carbon dioxide, by adding additional charges of cleaning chemicals, or a combination thereof. In addition, each repeat of steps 504 and 506 may include changing the type of processing fluid, for example, changing from pure carbon dioxide fluid to carbon dioxide mixed with a cleaning chemical, or changing the type of cleaning chemical that is combined with the carbon dioxide, or eliminating the cleaning chemical to change to

a pure carbon dioxide fluid. By way of example only, the fluoro-carbon dielectric film on the substrate may be cleaned first with a supercritical carbon dioxide fluid containing an alcohol, such as methanol, and then cleaned again with a supercritical carbon dioxide fluid containing a silicon-containing chemical, such as hexamethyldisilane. Alternately, the fluoro-carbon dielectric film on the substrate may be cleaned with a supercritical carbon dioxide fluid containing both an alcohol and a silicon-containing chemical.

[Para 53] Still referring to FIG. 5, after the cleaning process or cycles containing steps 504 - 508 is complete, the substrate can be treated with a supercritical carbon dioxide rinse solution in step 510. The supercritical carbon dioxide rinsing solution can contain supercritical carbon dioxide fluid and one or more organic solvents, for example an alcohol or a ketone, but can also be pure supercritical carbon dioxide. After the substrate is cleaned in the steps 504 - 508 and rinsed in the step 510, the process chamber is depressurized and the substrate is removed from the process chamber in step 512. Alternately, the substrate can be cycled through one or more additional cleaning/rinse processes comprising the steps 504-510, as indicated by the arrow connecting the steps 510 and 504 in the flow diagram. Alternately, or in addition to cycling the substrate through one or more additional cleaning/rinse cycles, the substrate can be treated to several rinse cycles prior to removing the substrate from the process chamber in step 512, as indicated by the arrow connecting the steps 510 and 508.

[Para 54] It will be clear to one skilled in the art of supercritical fluid processing that any number of different treatment sequences are within the scope of the invention. For example, cleaning steps and rinsing steps can be combined in any number of different ways to facilitate the removal of contaminants from a fluoro-carbon dielectric film. Furthermore, it would be appreciated by those skilled in the art, each of the steps or stages in the flowchart of FIG. 5 may encompass one or more separate steps and/or operations. Accordingly, the recitation of only seven steps in 502, 504, 506, 508, 510, 512 should not be understood to be limited solely to seven steps or stages. Moreover, each representative step or stage 502, 504, 506, 508, 510, 512 should not be understood to be limited to only a single process.

EXAMPLE: Supercritical Carbon Dioxide Processing of Fluoro-carbon Dielectric Films

[Para 55] A first batch of substrates included 200 mm Si wafers containing fluoro-carbon dielectric films on the Si wafers. A second batch of substrates contained 200

mm Si wafers containing nitrogen-incorporated fluoro-carbon dielectric films on the Si wafers. Reference will now be made to the pressure diagram in FIG. 4.

[Para 56] In a first supercritical carbon dioxide process flow, the above-mentioned first and second batches of substrates were processed for 2 min (T_2) at a process pressure (P_{op}) of 2,700 psig using a supercritical carbon dioxide fluid containing pure supercritical carbon dioxide. The processing further included three decompression – compression cycles (T_4) at pressures between 2,700 psig and 1,600 psig.

[Para 57] In a second supercritical carbon dioxide process flow, new first and second batches of substrates were processed for 2 min (T_2) at a process pressure (P_{op}) of 2,800 psig using a supercritical carbon dioxide fluid containing methanol (MeOH) solvent. The methanol solvent was injected at a process pressure of 2,300 psig. The processing further included a 2 min (T_3) push-through process at 2,950 psig, and five decompression-compression cycles (T_4) at pressures between 2,900 psig and 2,300 psig. Next, further processing was performed on the substrates for 2 min at a process pressure of 2,800 psig using a pure supercritical carbon dioxide fluid, followed by a 2 min push-through process at a pressure of 2,950 psig, and one decompression-compression cycle at pressures between 2,900 psig and 2,300 psig. Next, still further processing was performed for 2 min at a process pressure of 2,800 psig using a supercritical carbon dioxide fluid containing hexamethyldisilane (HMDS) solvent. The HMDS solvent was injected at a process pressure of 2,300 psig. The processing further included a 2 min push-through process at 2,950 psig, and five decompression-compression cycles at pressures between 2,900 psig and 2,300 psig.

[Para 58] FIG. 6 shows electrical resistance measurements of film structures containing tantalum films deposited onto fluoro-carbon dielectric films processed according to embodiments of the present invention. The fluoro-carbon dielectric films were processed according to the above first and second process flow prior to deposition of the tantalum films onto the fluoro-carbon dielectric films. The tantalum films were deposited onto the fluoro-carbon dielectric films by physical vapor deposition at a substrate temperature of 250°C and were about 200 Å thick. The electrical resistance measurements were performed before and after annealing the film structures in 2 Torr of Ar gas for 30 min at a substrate temperature of 400°C. The electrical resistance was measured in the center of the 200 mm wafers.

[Para 59] The electrical resistance measurements in FIG. 6 show that the electrical resistance of the film structures generally increased upon the annealing at 400°C. However, unexpectedly, the film structures containing fluoro-carbon dielectric layers

that were processed using supercritical carbon dioxide fluids containing methanol and hexamethyldisilane, showed minimal increase in the measured electrical resistance upon annealing. It is believed that the supercritical carbon dioxide processing using methanol and hexamethyldisilane effectively cleans contaminants from the exposed surface of the fluoro-carbon dielectric film and forms a surface termination layer containing Si-CH_3 functional groups that reduces chemical reaction of the tantalum film with the fluoro-carbon dielectric film during the annealing at 400ºC. Also, although not shown, processing with pure supercritical carbon dioxide fluid provided a significant improvement in electrical properties versus untreated film structures.

[Para 60] While the present invention has been described in terms of specific embodiments incorporating details to facilitate the understanding of the principles of construction and operation of the invention, such references herein to specific embodiments and details thereof are not intended to limit the scope of the claims appended hereto. It will be apparent to those skilled in the art that modifications may be made in the embodiments chosen for illustration without departing from the spirit and scope of the invention.